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Decay and thermoluminescence studies of CaS: Nd phosphors

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Phosphorescence decay characteristics (PDC) of CaS . Nd microcrystalline phosphors are studied at room temperature, 302°K; and trap depth is evaluated by peeling off the log $I-t$ curves The value of trap depth also calculated by Curie formula of thermoluminescence (TL) resembles with that calculated from PDC to a good approximation. Variation in decay constant with Nd-concentration shows a fair agreement with the results of flourescence The results obtained in the present investigation are in consonance with the theory of Randall & Wilkins and give consistent interpretation in favour of the kinetics of after-glow.

1 Introduction

The knowledge of defect structures and its connection with distribution of energy levels in the band gap of solids is an important prerequisite for the thorough understanding of luminescence phenomenon. Rare earth activated alkaline earth sulphide phosphors have attracted the attention of various workers in recent years. In the present work an attempt has been made to understand the luminescent nature of CaS · Nd phosphors and to know the decay law, the type of kinetics involved and the distribution of trap levels through phosphorescence decay characteristics (PDC) and also through thermoluminescence (TL) studies.

2. Experimental

Preparation of phosphors

Following Bhawalkar's method (Bhawalkar 1951) clean transparent pieces of gypsum are taken. They are finely powdered to the grain size of about 200μ and purified by nitric acid treatment This powder is termed as host. Likewise, the reducing agent carbon is also purified. Host and carbon are mixed in the ratio of 5·1 and fluxed with A.R. grade hypo taken equal to the weight of carbon. To an intimate mixture of these the varying amount of activator neodymium is added and this charge is fired at 930 $\pm$10°C for two hours. Finally it is pulvarised and collected as phosphor.

Measurement of decay and thermoluminescence

In the present case the studies of PDC and TL are made on the apparatus used by Machwe (Machwe 1969) and Verma & Bhawalkar (1971) respectively. The phosphors are excited by 3650Å radiations at room temperature of 302°K. The emitted luminescence is recorded in arbitrary units in terms of the deflections of Tinsley galvanometer (sensitivity 10^{-9} amp /mm) which is connected via a IP21 photo-multiplier tube.

In case of PDC, just after the excitation is cut-off, the decreasing deflection with increasing time is recorded

In case of TL the excited phosphors are first allowed to decay out to the same low value (here a fixed galvanometer reading) and then heated above room temperature by constant warming rate. The rate is carefully determined from calibration curves The phosphor glow increases with the rise of temperature to a certain limit and then decreases Such a change in glow with temperature is recorded for TL.

Results of PDC

Decaying intensity I is plotted against time t. Such a plot termed as PDC shows a fast decline of intensity followed by slow one Further $\log I$ is plotted versus t in Figure 1 It is not a satraight line and hence indicates non-exponential decay of these phosphors The $\log I$—$\log t$ plots (figure 2) show almost linearity

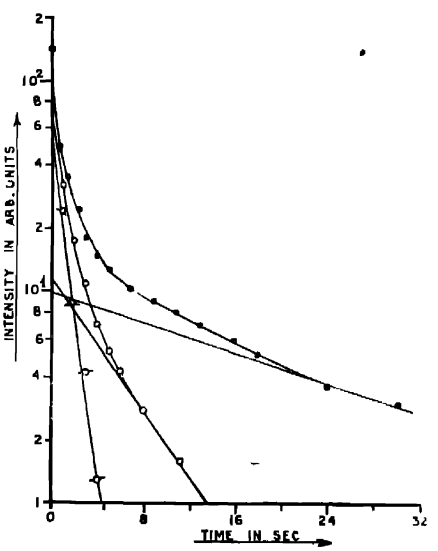

Fig 1. Log I—t plot (curve) peeled-off. X-axis ..time in sec. Y-axis ..intensity in arbitrary units.

which helps in concluding that the PDC is hyperbolic in nature. The degree of linearity is therefore estimated by evaluating correlation coefficient r (Agnihotri & Ranade 1968), the values of which are close to unity. They are given in Table 1. Such type of PDC can be represented by a power law as suggested by Randall & Wilkins (1945a) They considered hyperbolic decay as the result of superposition

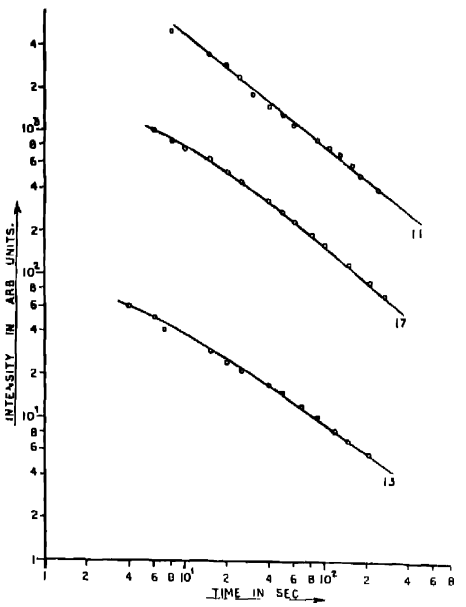

Fig 2. Log I—log t plots for CaS:Nd Phosphors. X-axis time in sec, Y-axis intensity in arbitrary units

of exponentials corresponding to different traps By peeling-off procedure as suggested by Bube (1950), it is possible to break up the log I–t decay curve into three different components, as shown in figure 1 Corresponding to these components three different trap depths are obtained by using the following equations :

$$\text{and} \qquad \begin{aligned} I &= I_0 \exp(-pt) \qquad \text{...(a)} \\ p &= s \exp(-E/kT), \qquad \text{.(b)} \end{aligned} \qquad \ldots (1)$$

where p is the probability of escape of electrons from traps per sec , s is attempt to escape frequency or frequency factor (here 10^9/sec.), E is trap depth, k the Boltzmann constant and T the temperature in °K. The values of E thus calculated are tabulated in Table 1, and later on termed as slow, middle and fast.

Table 1. Values of trap depth, correlation coefficient and decay constant calculated from PDC

Sl No	Sample No.	Conc of Nd in 10 gms of $CaSO_4$ (in gms)	Trap depth in eV			Correlation coefficient r	Decay constant b
			E_1 (Slow)	E_2 (Middle)	E_3 (Fast)		
1	9	2.0×10^{-4}	0.641	0 596	0.550	1 03	0 69
2	10	$3\ 0\times10^{-4}$	0 636	0 607	0.555	1 01	0 71
3	11	$6\ 0\times10^{-4}$	0.671	0 634	0 591	0.98	0 71
4	12	$7\ 0\times10^{-4}$	0 644	0 609	0 560	0 95	0 73
5	13	$8\ 0\times10^{-4}$	0 680	0 621	0.604	0 99	0 73
6	14	$9\ 0\times10^{-4}$	0 681	0 629	0.601	0 91	0 61
7	15	$1\ 0\times10^{-3}$	0 665	0 613	0 591	0 99	0.57
8	17	3.21×10^{-3}	0 672	0 630	0 600	—	0 60
9	18	$4\ 28\times10^{-3}$	0 669	0 614	0 579	0 56	0 48
10	20	$7\ 5\times10^{-3}$	0 673	0 619	0 589	0 95	0 62
11	21	1.0×10^{-2}	0 662	0.598	0 569	0 99	0 91
12	22	$2\ 0\times10^{-2}$	0 646	0.596	0.562	0 91	0 77
13	23	$1\ 5\times10^{-2}$	0.678	0 619	0 586	0 97	0 77
14	24	$5\ 0\times10^{-2}$	0 631	0.582	0 553	—	—
15	26	$8\ 0\times10^{-2}$	0.655	0.593	0 566	0 98	0 54
16	27	$1\ 0\times10^{-1}$	0 581	0 529	—	0 98	0 44

Results of TL

TL curves for a number of phosphors are plotted as glowing I versus rising T (figure 3) for three warming rates, $\beta_1 = 0.275$, $\beta_2 = 0\ 590$ and $\beta_3 = 0\ 720$ degree per sec. Corresponding to these three β's the glow peak intensities T_g's are obtained. The values of E for all the samples are calculated by two formulae given below : one by Randall & Wilkins (1945b)

$$E(ev) = kT_g \log s = 20.73\ kT_g. \tag{2}$$

and the other by Curie (1963)

$$E(ev) = \frac{T_g(^\circ\mathrm{K}) - T_0(\beta/s)}{K(\beta/s)} \tag{3}$$

where the values of T_0 and K are obtained graphically for various sets of $\theta = \beta/s$. The values of E are shown in the table 2.

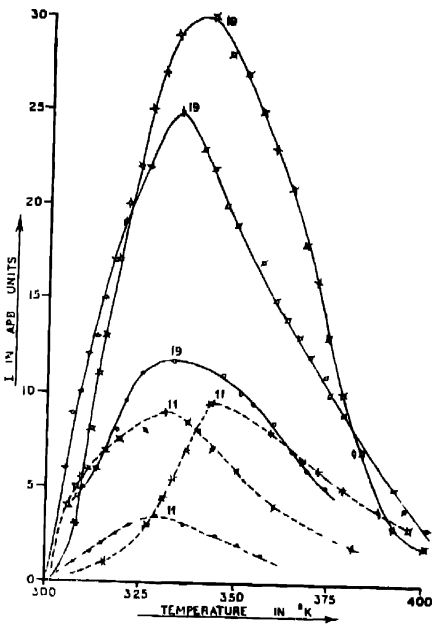

Fig 3 T versus I plots of TL for CaS:Nd. Heating rates are β_1 0 275 °K/sec, β_2 = 0.597 °K/sec, β_3 = 0 72°K/sec X-axis temperature in °K. Y-axis I in arbitrary units.

Table 2 Values of trap depth from TL-studies as calculated by three heating rates, viz;
$\beta_1 = 0.273$°K/sec., $\beta_2 = 0.597$°K/sec. and $\beta_3 = 0.720$°K/sec.

No.	Sample No	E(ev) from Curie's Formula			E(ev) from Randall & Wilkins Formula		
		β_1	β_2	β_3	β_1	β_2	β_3
1	11	0 7122	0 7003	0 7157	0 5862	0 5916	0 6112
2	12	0.7188	0 7122	0.7383	0 5916	0.6016	0 6244
3	13	0 7089	0 6829	0 7071	0.5833	0 5809	0 6039
4	14	0 7155	0.6971	0.7079	0 5887	0.5887	0 6059
5	15	0 7173	0 6895	0 7499	0.5906	0.5826	0.6397
6	16	0 7155	0 7174	0 7157	0 5887	0 5823	0 6112
7	17		0 7360	0.7433	-	0.6210	0.6342
8	18	0 7188	0 6992	0.7136	0 5916	0.5906	0 6094
9	19	0 7211	0.7057	0 7157	0 5942	0 5960	0.6112
10	20	0 7081	0.6982	0.6879	0 5830	0 5898	0 5882

3. Discussion

The eq 1(b) due to Randall & Wilkins is of fundamental importance. The roll of traps seeks attention in long duration phosphorescence and TL as an inherent mechanism Reports about short lived traps causing exponential PDC are commonly found. Usually, for a single trap depth the eq. 1(b) depends on assumptions . (a) ejection of electrons is the only rate determining processes. and (b) radiationless transitions and probability of retrapping are negligible. It represents a purely exponential decay Theoretical and experimental studies on KCl.Tl type of non-photoconducting phosphors (Williams 1951) obey such a decay law. Further as the number of exponentially distributed traps increases, the decay takes the form of hyperbolic nature due to their superposition. The minimum number of exponentials required to do so can be three as suggested by Bube In the present case such an analysis appears to be true Superposition of trapping levels at different energies makes the emission complicated. If the decay obeys first order kinetics, for more than one trap depths the decay can be given by modifying eq. (1) in the activation energy range of E and $E+dE$ for $N_e\,dE$ number of traps as below · (Randall & Wilkins, 1945a)

$$I = \int_0^\infty N_e.s \exp(-E/kT) \exp\{-st \exp(-E/kT)\}dE$$

or,

$$I = \frac{N_e\, s}{\exp(st)} \int_0^\infty \exp(-E/kT) \exp\{\exp(-E/kT)\}dE \qquad \ldots (4)$$

For a uniform distribution where N_e is constant and for $t >> s^{-1}$, the second term of the exponential reduces to kT and the first term to N_e/kT, and hence

$$I \approx \frac{N_e kT}{t} \approx \frac{\text{constant}}{t} \qquad \ldots (5)$$

It has been observed that such a decay law also does not hold good in the present case because I versus $1/t$ plots are not straight lines As a consequence a kind of power law can be thought over. Before concluding to any power law it is tried to investigate the applicability of the bimolecular law (Mott & Gurney, 1964)

$$1/(I)^{\frac{1}{2}} = 1/(I_0)^{\frac{1}{2}}.(1+An_0t) \qquad \ldots (6)$$

where A is a constant and n_0 the number of recombining electrons at $t = 0$ The plots of $1(I)^{\frac{1}{2}}$ versus t (Figure 4), are not linear Finally a power law decay of the form (Sinha & Sivaraman 1971, Lawanger & Narlikar 1972)

$$I = I_0 t^{-b} \qquad \ldots (7)$$

is found to be applicable where b represents the decay constant which is the slope of the log I—log t line The value of b is calculated by the method of least squares (Muley 1969) It lies between 0 44 to 0 91 (table 1) Its average value, *i e*, 0 66 is much less than unity and hence the distribution of traps is reported to be *quasi uniform* (Lawenger & Narlikar 1972) The average values of E for slow, middle and fast groups of exponentials are 0.657 *ev*, 0 605*ev* and 0.544 *ev* respectively.

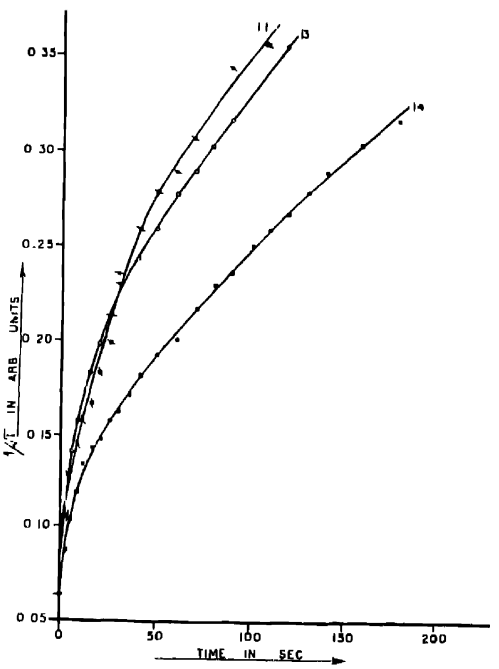

Fig 4 t versus $1/(I)^{\frac{1}{2}}$ plots for CaS:Nd phosphors. X-axis time in sec ; Y-axis $1/(I)^{\frac{1}{2}}$ in arbitrary units

The calculations of E the activation energy, are also made by TL results Limitations of this method are the control over uniform heating rate and determination of T_g. In the present case these heating rates are not taken very close to each other The variation of T_g's for the three β's are fairly uniform and consistent within the experimental means The T_g variation for β_1, β_2 and β_3 is 7°K, 22°K and 29°K respectively The values of E as calculated by eq (3) for all the three values of β are also uniform and almost same The average value is 0 77 ev approximately. This value is slightly higher than the slowest component decay which suggests that evacuation of deeper traps is easy by thermal stimulation However, the value of E calculated by eq (2), which is also used by many workers (Sivaraman & Bhawalkar 1971, Agnihotri & Ranade 1968) shows a slight variation

and low limit with the change in (table 2). The average value of 0.59 ev for E corresponds to the fast component of the decay. It is quite reasonable because the related expression for E appears only after assuming that the factor $\{1+f(s,\beta)\}$ is unity for $f(s,\beta) \ll 1$. Again because the formula due to Curie is numerically obtained with 1% accuracy, it is used here and the values of E so obtained are compared with those obtained by the Randall & Wilkins formula They are within the permissible range and almost same. Curie formula has also been used by many workers (Sharma & Singh 1969, Pathak & Kamra 1972) To be more fair in predicting this finally, the values of E were also calculated by the formulae suggested by Booth (1954), Grossweiner (1953), and Halperin & Braner (1960) They are not reported here because the variation lies between 0.52 ev to 0.96 ev Such deviations are quite natural also because the experimental technique followed by these workers differed much with the present one

Variation of decay constant with activator concentration

The graph between activator concentration in wt percent and decay constant b is shown in Figure 5. Initially there appears only one fluorencence band at 0.002% of Nd (the fluorescence spectra are not reported). As the concentration increases up to 0.008% of Nd, the value of b also increases Further b decreases rapidly and reaches to as low as 0.44 when Nd becomes 0.0428% This seems because of the distribution of the energy of bands into separate and distinct lines On increasing the concentration still above to this value, fall in line intensities and rise in the value of b occur Ultimately as the stage of *concentration quenching* at 1.0% of Nd occurs, the value of b declines. Variation of b with activator concentration is reported also by Bhawalkar & Malhotra (1969) and Sinha & Sivaraman (1971)

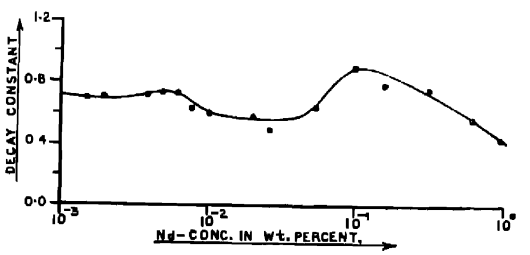

Fig 5 Curve of Nd concentration versus decay constant. X-axis . Nd conc. in wt percent Y-axis .decay constant

4. Conclusions

In the last it can be concluded that the theory of Randall & Wilkins helps in assuming the power law $I = I_0 t^{-b}$. is true for the PDC Though the bimolecular kinetics with hyperbolic decay goes well but it being the superposition of

more than one monomolecular processes, ultimately monomolecular kinetics can probably be assigned to the present type of decay

Retrapping seems to be of no importance in these phosphors in the same manner as reported by Garlick & Gibson (1948) For TL the formula used by Curie should better be applied. The decay constant variation with activator concentration implies proper growth of microcrystalline powder phosphors. The value of E does not depend on the concentration of the activator. The TL curves do not show any *shoulder* and hence more than one traps are not revealed up to 410°K by the applied heating rates Traps are seen to be associated with defects or to native lattice rather than the activator alone which seems to modify the trap distribution (Bube 1953) or change the form of the glow curve (Alder 1959). Thus the non-characteristic type of luminescence can be assigned to the present series of phosphors.

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